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Particle-water interactions of bismuth under simulated estuarine conditions

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Abstract

Although the production and usage of bismuth (Bi) have been increasing, very little is known about the environmental behaviour of this heavy metal. In the present study, the particle-water interactions of Bi are examined under controlled conditions in which the metal is added as a tracer to estuarine sediment suspended in different, environmentally-relevant aqueous solutions. Adsorption isotherms were always linear over the Bi concentration range employed (up to 2000 μg L^{-1}) and sediment-water distribution coefficients derived from isotherm gradients, K_D (L kg^{-1}), displayed an inverse dependence on pH in river water (and ranging from K_D = 106,000 L kg^{-1} at pH 5.0 to K_D = 17,700 L kg^{-1} at pH 9.0) that were consistent with the adsorption of hydroxo-complexes to the sediment surface. Higher adsorption in ultra-pure water of the same pH as river water and an order of magnitude increase in adsorption in seawater at pH 8.0 (K_D = 1,530,000 L kg^{-1}) and 0.7 M $NaNO_3$ at pH 6.5 (K_D = 4,290,000 L kg^{-1}), however, required the presence of additional species or processes that are likely related to organic complexation of the metal. Thus, experiments conducted in mixtures of river water and seawater in the absence of sediment suggested that Bi may also be bound to colloidal organic molecules that undergo flocculation and salting out on estuarine mixing. Compared with other metals studied under similar conditions, Bi displays a high reactivity towards sediment particles and is, therefore, predicted to be retained in estuaries to a significant extent from catchment sources.

Keywords: bismuth; adsorption; rivers; estuaries; sediment; flocculation

1. **Introduction**

Bismuth is the heaviest element in Group 15 of the Periodic Table whose only naturally occurring isotope (^{209}Bi) is extremely weakly radioactive and decays with a half-life of about 2 x 10^{19} years (Beeman et al., 2012). Bismuth is widely distributed in the environment with an average crustal abundance of 0.2 ppm (Das et al., 2006) but also occurs in bismite (Bi_2O_3) and bismuthinite (Bi_2S_3) from which it may be obtained as a by-product of copper and lead ores (Ayres and Hellier, 1998). Although Bi can exist in a number of oxidation states, the trivalent form is the most stable in the environment; this contrasts with the Group 15 metalloids, As and Sb, whose most stable state is the pentavalent (Filella, 2010).

Bismuth has no known biological role and is believed to be the least toxic heavy metal to humans, although some toxicity is exhibited towards certain bacteria and macroalgae (Kearns and Turner, 2016). Its antibacterial properties have been exploited in pharmaceutical products treating bacterial

infections as well as medications treating ulcers and gastrointestinal disorders (Tremaine, 2000; Kotani et al., 2005). Bismuth and its compounds are also used in cosmetics, paints, fusible alloys, catalysts and semiconductors (Ayres and Hellier, 1998), and recently Bi has gained popularity as a non-toxic replacement for lead in upland and waterfowl hunting shot (Fahay et al., 2008).

Despite these applications and a sharp increase in the recent global production of Bi to over 13,000 tonnes in 2015 (Kelly and Matos, 2017), there exists very little information on the environmental behaviour of the metal. Filella (2010) suggests that this is due to low concentrations in the environment, often attributed to the insolubility of its compounds, and low toxicity to humans. Her review of concentrations of Bi in natural waters revealed a wide dispersion of values (but usually < 1 $\mu g\ L^{-1}$), which can be partly accounted for by external contamination during sampling and analysis and by lack of information provided on whether or how samples were filtered. Moreover, an examination of stability constants used in aqueous speciation calculations were found to be indirectly sourced from a limited number of old references, one of which when translated from Russian was found to contain an important error that was subsequently reproduced in the key reference work of Ahrens (1968). Filella (2010) also suggests that no studies of Bi adsorption to heterogeneous solids had been undertaken and that the metal had been overlooked in sorption constant estimations derived from free energy regressions. To our knowledge, the only adsorption experiments conducted with Bi are reported by Ulrich and Dedueidre (1993). Here, the interactions of ^{210}Bi (as a radiotracer) with montmorillonite clay were examined under varying conditions of pH and ionic strength. Distribution coefficients derived from adsorbed to aqueous concentration ratios and ranging from 10^4 to 10^7 L kg^{-1} were later employed by Serne (2007) in order to evaluate the fate, transport and risk of Bi in agricultural soils and river bank sediments.

Because of the dearth of information on the behaviour of Bi in the natural environment, the present study set out to systematically examine the adsorption of the metal to estuarine sediment under different conditions of pH, ionic composition and salinity. The study employs protocols that we have adopted before and relies on the addition of the metal as a tracer to aqueous suspensions and at concentrations that are detectable by quadrupole ICP-MS (Turner, 2007; Turner et al., 2010). The sorption constants derived will enable the transport and fate of Bi to be evaluated and modelled more accurately in rivers and estuaries, and will improve our more general understanding of the behaviour of Bi in the aquatic environment.

2. Methods

78 *2.1. Sampling*

79 River water used in the experiments was collected on a weekly basis between May and July 2019 in a
80 5-L high density polyethylene carboy from the Erme near Ivybridge, southwest England (50.388313, -
81 3.9215163). Here, the bed profile is of low permeability, being comprised of large granite boulders
82 derived from the protected moorland of central southern Dartmoor (a National Park), and average
83 river flow is 1.95 $m^3 s^{-1}$ (National Flow River Archive, 2017). About 0.5 kg of surficial, oxic sediment
84 from the protected saltmarshes of the upper Erme estuary (50.332221, -3.9337894) was sampled
85 using a tapered plastic spatula and stored in a zip-locked polyethylene bag. Seawater was available
86 on tap in the laboratory having been previously collected in bulk from the English Channel.

87

88 *2.2. Sample processing and characterisation*

89 River water and seawater were vacuum-filtered through 0.45 μm cellulose acetate filters into a
90 series of acid-cleaned 1-L polyethylene bottles and used within 24 hours. Estuarine sediment was
91 sieved through a 63 μm nylon mesh with the aid of filtered river water and transferred to a series of
92 50 mL Fisherbrand screw-capped polypropylene centrifuge tubes. The contents of each tube were
93 centrifuged for 20 minutes at 3500 rpm before supernatants were poured off and remaining
94 sediment frozen until required.

95 The pH and conductivity (hence salinity) of aqueous samples were determined using colour-fixed
96 indicator sticks or a Jenway 3305 probe and a YSI 85 conductivity meter, respectively. The presence
97 of Bi was checked by inductively coupled plasma-mass spectrometry (ICP-MS; see below) after 10 mL
98 of filtered river water had been spiked with 100 μL of concentrated HCl (VWR ARISTAR) and 2 ml of
99 filtered seawater had been diluted to 10 mL with 1M HCl. A subsample of fractionated sediment was
100 thawed out and homogenised using a plastic spatula before ~ 1 g aliquots were used to determine
101 moisture content on drying at 105 ^{o}C for 24 hours, loss on ignition after combustion at 550^{o}C for 4
102 hours, and mean particle diameter using a Malvern Instruments Hydro 2000G Mastersizer. In
103 triplicate, 0.5 g of dried sediment and 0.25 g of a certified reference sample (SS-2 Contaminated Soil,
104 140-025-002) were digested in 10 mL of boiling aqua regia (VWR ARISTAR HCl and HNO_3) in 50 mL
105 Pyrex beakers covered with watch glasses; controls were performed likewise but in the absence of
106 solids. The cooled digests were filtered through Whatman 85 g m^{-2} acid-resistant circles and diluted
107 to 50 mL with Millipore Milli-Q water (MQW). Concentrations of Bi and a suite of other elements
108 were determined in the diluted digests by ICP-MS (see below).

109

2.3. Adsorption experiments

The general approach for the adsorption isotherm experiments was adapted from Turner et al. (2010) as follows. A 100 mg L^{-1} working solution of Bi was prepared in a 50 mL volumetric flask by diluting 500 μL of 10,000 mg L^{-1} Bi standard (VWR ARISTAR) in filtered river water. Meanwhile, a slurry stock of ~ 4 g dry sediment L^{-1} was prepared by adding 0.5 ± 0.05 g of thawed sediment to 50 mL of filtered river water in a volumetric flask. To a series of screw-capped 50 mL polypropylene centrifuge tubes, 1 mL of slurry stock was diluted in 40 mL of river or sea water to give a particulate concentration on a dry weight basis of ~ 100 mg L^{-1}. Bismuth was pipetted to the centrifuge tubes from the working standard to produce a concentration series ranging from 10 to 2000 μg L^{-1}, with two concentrations in each isotherm performed in triplicate. The centrifuge tubes were subsequently agitated at room temperature (~ 20 °C) and in the dark in the horizontal position on a lateral shaker for 16-18 h at 100 rpm. Following incubation, particulate and aqueous phases were separated by vacuum-filtration through 0.45 μm cellulose acetate membranes. Ten mL filtrate aliquots were transferred to 30 mL Thermo Scientific polystyrene Sterilin tubes and acidified with 100 μl of concentrated HCl. Filters were transferred to Sterilin tubes and Bi was extracted for 18 h in 10 mL of 1M HCl and 10 mL of 1M HNO_3.

This process was repeated using MQW in place of river water, and after adjusting (and, if necessary, maintaining) the pH of river water to 5 and 9 by dropwise addition of 1M HNO_3 and 1M NaOH, respectively. Experiments were also repeated in seawater and using solutions of 0.7 M NaCl (Fisher Scientific Extra Pure) and 0.7 M $NaNO_3$ (VWR AnalaR) but with 4 mL filtrates diluted to 20 mL in 1M HCl. Bismuth adsorption was also studied at a single concentration (1000 μg L^{-1}) across the estuarine gradient in 50 mL solutions of salinities 0, 2, 5, 10, 15, 20 and 30 created by mixing filtered river water and filtered seawater end-members in different proportions. This process was also repeated in the absence of sediment in order to evaluate the extent of flocculation and filter adsorption of the metal. To assess the significance of container adsorption, the emptied centrifuge tubes arising from various experiments and different added Bi concentrations were extracted with 25 mL of 20% HNO_3 for 16-18 h under lateral agitation at 100 rpm.

2.4. ICP-MS analysis

Acidified and diluted filtrates, filter extracts, centrifuge tube extracts, and sediment digests and controls (and any dilutions thereof) were analysed in triplicate for Bi (and, for sediment digests, Al, As, Ca, Fe, Mn and Sb) by ICP-MS using a Thermo Scientific iCAP TQ with a concentric glass nebuliser and cyclone spray chamber. The instrument was calibrated using blanks and standards of 1, 4, 10, 40, 100 and 400 μg L^{-1} prepared in either 2% HNO_3 or diluted and acidified sea water, while internal

standardisation was achieved by addition of 20 μg L^{-1} of Ir to all samples and standards. Instrument drift was monitored with standard checks after every ten samples, with reanalysis performed if deviation of more than 10% from the expected value occurred. Elemental concentrations returned for the certified reference soil were within stated tolerance intervals with the exception of Bi (no natural geosolid appears to be certified with respect to this metal). Under conditions where Bi adsorption was replicated (*n* = 3), precision, as relative standard deviation, ranged from 5.1 to 28.2% (median = 12.6%) for the aqueous phase and 2.3 to 46.4% (median 12.5%) for filter extracts.

3. Results

3.1. Sample characteristics

The pH of filtered Erme river water used in the experiments ranged from 6.2 to 6.5, while conductivity varied from 63.5 to 107 μS cm^{-1}, and the pH and salinity of filtered English Channel seawater were 8.0 and 30.8, respectively. Although dissolved organic matter was not determined in the aqueous samples, previous measurements of dissolved organic carbon performed in adjacent rivers draining the same region of Dartmoor and in the local coastal region of the English Channel indicate typical values of about 1.7 and 1.4 mg L^{-1}, respectively (Rawling et al., 1998). The mean, background concentration of Bi in river water was 0.28 $\pm$ 0.01 μg L^{-1} but in seawater the metal was below the detection limit of < 0.05 μg L^{-1}.

The fractionated estuarine sediment use in the experiments had a median particle size of 19.3 μm and a moisture content of 59.9%, with a combustible mass when dry (i.e. organic content) of 13.3%. Dry weight concentrations of Al, Ca, Fe and Mn (in μg g^{-1} and as the mean $\pm$ one standard deviation of three determinations) were 17,500 $\pm$ 185, 2670 $\pm$ 9.1, 41,700 $\pm$ 97.1 and 332 $\pm$ 2.54, respectively, while concentrations of Bi and the other group VA elements, As and Sb, were 0.23 $\pm$ 0.09, 2.49 $\pm$ 0.86 and 3.12 $\pm$ 0.35, respectively.

3.2. Container adsorption

Although the aims of the study were to define the adsorption characteristics of Bi to estuarine sediment, it is useful, more generally, to understand how the metal behaves under controlled and contained laboratory conditions, and in particular whether there is any loss to non-environmental phases such as the reactor vessel or filter membrane. Mass balance considerations from the isotherm experiments revealed average percentages of added Bi that could not be accounted for in the sediment and aqueous phases ranging from about 26 to 64 (Table 1) but there was no clear relationship with the pH or ionic strength of the solution or the quantity of Bi added. Subsequent acid-washing of selected emptied centrifuge tubes revealed that the majority of Bi lost had

undergone heterogeneous adsorption to container surfaces, with analysis of filters arising from experiments conducted in the absence of sediment revealing additional loss of the metal to the membranes but not quantitatively attaining complete mass balance. Thus, it is critical to measure the distribution of Bi in all environmental phases considered in laboratory experiments as estimates relying on difference would lead to significant errors in constants defining adsorption processes.

3.2. Adsorption isotherms

Isotherms for Bi adsorption to fractionated estuarine sediment are shown for MQW at pH 6.5 and river water over a range of pH values in Figure 1. Here, concentrations of Bi extracted from sediment and normalised to dry mass, $[Bi]_{ads}$, are shown as a function of Bi concentrations measured in the aqueous phase, $[Bi]_{aq}$, after a 16-18 h incubation period. Note that in MQW, the full data set is not shown as the higher concentrations of added Bi were accompanied by significant shifts in aqueous pH. Isotherms were best defined by a linear model in all cases, with slopes of the relationships used to derive the sediment-water distribution coefficients, K_D (in L kg^{-1}):

$$K_D = [Bi]_{ads} * 10^3 / [Bi]_{aq}$$

shown in Table 2. Adsorption of Bi increases with a reduction in pH and from a K_D of 17,700 L kg^{-1} at pH 9.0 to a K_D of 106,000 L kg^{-1} at pH 5.0, but amongst all freshwater media is greatest in MQW (K_D = 113,000 L kg^{-1}) in which contaminant ions and organic matter are absent.

Adsorption isotherms are shown for seawater at pH 8.0 and for aqueous solutions of NaCl and $NaNO_3$ of equivalent ionic strength (but lower pH) in Figure 2. Note here that aqueous concentrations, but not particulate concentrations, are considerably lower than those measured in freshwater above (despite no clear differences in Bi recovery amongst different media reported in Table 1). Consequently, isotherm slopes and values of K_D (shown in Table 2) are at least an order of magnitude higher than those derived in river water and MQW.

3.3. Particle-water interactions along the estuarine gradient

Values of K_D, derived from concentration ratios of Bi extracted from sediment to Bi measured in the aqueous phase and for an added Bi concentration of 1000 μg L^{-1}, are shown after logarithmic conversion as a function of salinity in Figure 3. Here, the *x*-axis represents the estuarine gradient, or the extent of mixing of river water and seawater end members. The logged K_D data exhibit a significant and positive linear relationship with salinity defined by a slope of 0.0615 and an intercept of about 4. In Figure 4, the percentage of Bi added at a concentration of 1000 μg L^{-1} that is retained by filtration but in the absence of estuarine sediment is shown along the estuarine gradient. Percentages are lowest at the end-members where they may be attributed to filter adsorption and,

possibly, precipitation, and are enhanced by end-member mixing, with values exceeding 70% in the mid-estuarine region.

4. Discussion

The findings of the present work indicate substantive loss of Bi to container surfaces, an effect that has been reported for glass and plastic in previous analytical and experimental studies of the metal in freshwater and seawater (Lee, 1982; Ulrich and Deguelde, 1993). Clearly, studies involving Bi as a tracer under contained experimental conditions require careful consideration of reactor adsorption and the direct analysis of all environmental phases involved. With respect to adsorption studies, it is critical that both particulate and aqueous Bi are measured and that derivation of concentrations does not rely on difference. Isotherms reported here and determined directly define the adsorption of Bi to fractionated estuarine sediment suspended in various environmentally relevant solutions and appear to be the first documented for this metal using a natural sorbent. That isotherms are linear suggests binding sites at the particle surface are not limited for Bi, at least over the concentration range studied, and adsorption constants derived are likely to be applicable at lower, more environmentally realistic concentrations of the metal.

Increasing adsorption of Bi (as K_D) with decreasing pH and increasing salinity are not consistent with the adsorption of metal cations to soils or sediment. Here, adsorption is predicted to increase with pH as binding sites become progressively deprotonated and to decrease with increasing salinity because of competitive adsorption with seawater cations and complexation seawater anions (Peng et al., 2003; Zwolsman et al., 1997). For Bi, therefore, additional or alternative adsorbing species appear to be significant in sediment-water suspensions under the conditions tested.

Unfortunately, the aqueous speciation of Bi is poorly understood, and relevant constants appear to have been taken, often indirectly or inappropriately, from old sources (Filella, 2010). What is known is that Bi^{3+} is stable under only strongly acidic conditions and with increasing pH there is an increase in the variety and abundance of hydroxo-complexes. Under near-neutral freshwater conditions similar to those adopted herein, calculations undertaken by Ulrich and Deguelde (1993) indicate that 99.9% of the metal should exist as $Bi(OH)_3$, with the remainder comprised of $Bi(OH)^{2+}$ and a vanishingly small quantity of free Bi^{3+}. The authors suggest that adsorption can be modelled as a series of quasi-irreversible complexation reactions that, with respect to the sediment surface, =X, can be written as follows:

$$=X\text{-}O\text{-}H + Bi(OH)_3 \longrightarrow =X\text{-}O\text{-}Bi(OH)_2 + H_2O \qquad (1)$$

239 $=X\text{-}O\text{-}H + Bi(OH)^{2+} \longrightarrow =X\text{-}O\text{-}Bi^{2+} + H_2O$ (2)

240 $=X\text{-}O\text{-}H + Bi^{3+} \longrightarrow =X\text{-}O\text{-}Bi^{2+} + H^{+}$ (3)

241 Presumably, the dependence of Bi adsorption on pH arises from shifts in the aqueous speciation of
242 the metal and differences in the complexation constants of each reaction. Specifically, higher
243 adsorption at pH 5 may be attributed to the greater relative abundance of Bi^{3+} and a relatively high
244 complexation constant for reaction 3, while lower adsorption at pH 9 may be attributed to the
245 greater relative abundance of $Bi(OH)_3$ and a relatively low complexation constant for reaction 1. The
246 neutral hydroxide is also likely to be subject to non-specific sorption to the hydrophobic container
247 surfaces and may explain the loss of Bi observed in the experiments.

248 In seawater, the same species, plus $Bi(OH)_4^-$, have been proposed (Byrne, 2002). Because of the
249 higher pH of seawater than MQW or river water, a reduction in adsorption with increasing salinity
250 would be predicted on the basis of the arguments above. However, an exponential increase in K_D
251 across the estuarine gradient (Figure 3) requires that additional species or processes are present. It
252 has been suggested that cationic chloro-complexes or oxychloro-complexes of high reactivity occur
253 in seawater (Bertine et al., 1996; Kabata-Pendias and Mukherjee, 2007) but similar adsorption of Bi
254 observed in solutions of NaCl and $NaNO_3$ shown in Figure 2 imply that the distribution of K_D across
255 the estuarine gradient may be related to ionic strength. Significantly, we note a doubling in
256 adsorption (as K_D) of Bi to montmorillonite from ionic strengths of 0.01 M to 0.2 M reported in Ulrich
257 and Degueldre (1993) although no explanation is proposed by the authors.

258 Although Bi is known to bind with functional groups on the surfaces of macroalgae (Kearns and
259 Turner, 2016), no information exists in the literature on the complexation of Bi by dissolved organic
260 ligands in the environment. The results presented here, however, suggest that the metal is able to
261 interact with dissolved organic matter in different ways. Thus, firstly, higher adsorption in MQW
262 than in river water at the same pH (Table 1) suggests that natural organic ligands compete with
263 adsorption sites on the sediment surface for aqueous Bi and act to stabilise a fraction of the metal in
264 solution. Secondly, the capture of significant quantities of Bi on filters arising from the mixing of end-
265 members in the absence of sediment (Figure 4) suggests that associations of Bi with macromolecular
266 organic matter in river water are destabilised by the addition of seawater ions and are subject to
267 flocculation or coagulation (Zwolsman et al., 1997; Windom et al., 1999). Thirdly, the exponential
268 increase in K_D with increasing salinity is consistent with a modified version of the Setschenow
269 equation and suggests that organic complexes of Bi may be subject to salting out through
270 electrostriction (Turner et al., 2001).

Despite uncertainties in the aqueous speciation of Bi and the mechanisms by which it interacts at the particle surface, it is clear that the metal has a high affinity for sediment compared with other metals. Figure 5 compares K_D values for Bi derived here with those for a variety of metals studied as tracers (including radiotracers) in suspensions of estuarine sediment from the Plym (adjacent to the Erme) in Plym river water and English Channel seawater undertaken under otherwise identical conditions. Thus, in river water K_D is greatest for Bi but similar in magnitude to values for Cd, Hg and Zn, while in seawater K_D is greatest for Bi among the metals by almost an order of magnitude. Bismuth is, therefore, highly particle active and estuaries are predicted to be important sinks for river borne sources of the metal. These assertions are consistent with an oceanic input of the metal that is believed to be dominated by an aoelian, and probably volcanic, pathway (Lee et al., 1985/1986), and an estimated oceanic residence time of only 20 years (Bertine et al., 1996).

5. Conclusions

Very limited thermodynamic or empirical information exists relating to the behaviour of Bi in the aquatic environment. Here, it has been shown that Bi, added as a tracer, has a high affinity for sediment suspended in natural and synthetic media, with sediment water distribution coefficients of about 70,000 L kg^{-1} in river water at pH 6.5 (and that display an inverse dependency on pH between 5.0 and 9.0) and 1,500,000 L kg^{-1} in sea water. Adsorption is attributed to the complexation of various species (believed to be mainly hydroxides) at the particle surface. Results also indicate that a significant fraction of added Bi undergoes flocculation when the salinity of river water is increased, suggesting that Bi has some affinity for organic molecules that are destabilised as the concentration of aqueous ions is increased. With an increase in the global production and usage of Bi, further studies that better define its aqueous speciation and environmental fate are called for.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the findings of the study.

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362 Zwolsman, J.J.G., Van Eck, B.T.M., Van der Weijden, C.H., 1997. Geochemistry of dissolved trace
363 metals (cadmium, copper, zinc) in the Scheldt estuary, southwestern Netherlands: Impact of
364 seasonal variability. Geochimica et Cosmochimica Acta 61, 1635-1652.

365 Table 1: Percentage of added Bi (as mean ± one standard deviation) that was unaccounted for in the
366 isotherm experiments conducted in suspensions of fractionated estuarine sediment suspended in
367 different aqueous solutions.

aqueous solution	pH	% unaccounted
MQW	6.5	35.2±10.7
river water	6.5	48.0±9.0
	9.0	39.6±15.0
	5.0	26.2±7.7
seawater	8.0	33.9±9.7
0.7 M $NaNO_3$	6.5	52.8±8.8
0.7 M NaCl	6.5	63.5±11.8

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371 Table 2: Sediment-water distribution coefficients defining the slopes of the isotherms in Figures 1
372 and 2 along with goodness of fits to the data (note that $p < 0.01$ in all cases).

aqueous solution	pH	K_D, L kg^{-1}	r^2
MQW	6.5	113,000	0.992
river water	6.5	68,100	0.968
	9.0	17,700	0.974
	5.0	106,000	0.907
seawater	8.0	1,530,000	0.872
0.7 M $NaNO_3$	6.5	4,290,000	0.995
0.7 M NaCl	6.5	3,170,000	0.994

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Figure 1: Isotherms for Bi adsorption to fractionated sediment suspended in different freshwater solutions. Solid lines denote best fits by linear regression analysis whose slopes (as K_D) and goodness of fits are shown in Table 2.

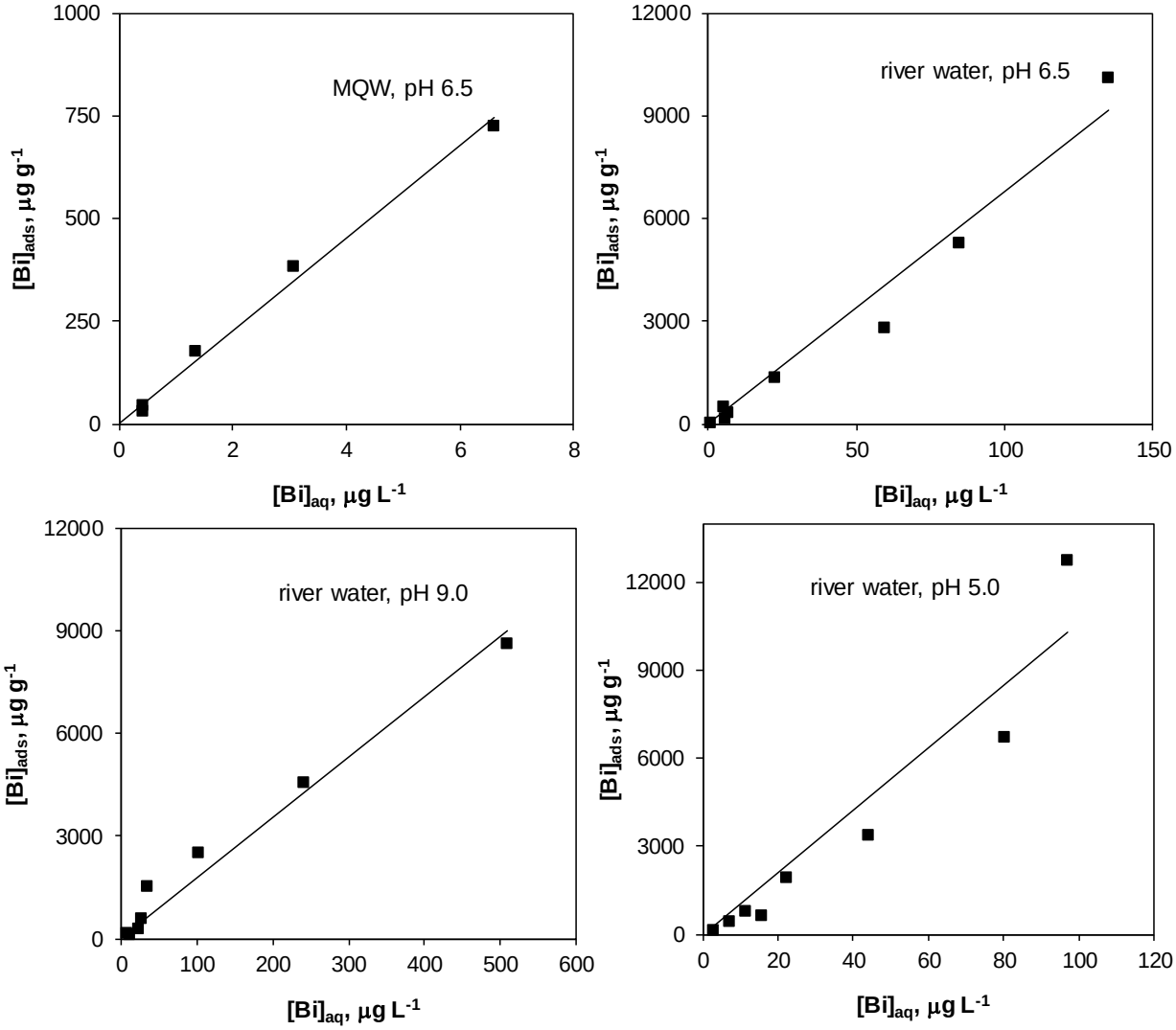

Figure 2: Isotherms for Bi adsorption to fractionated sediment suspended in different saline media. Solid lines denote best fits by linear regression analysis whose slopes (as K_D) and goodness of fits are shown in Table 2.

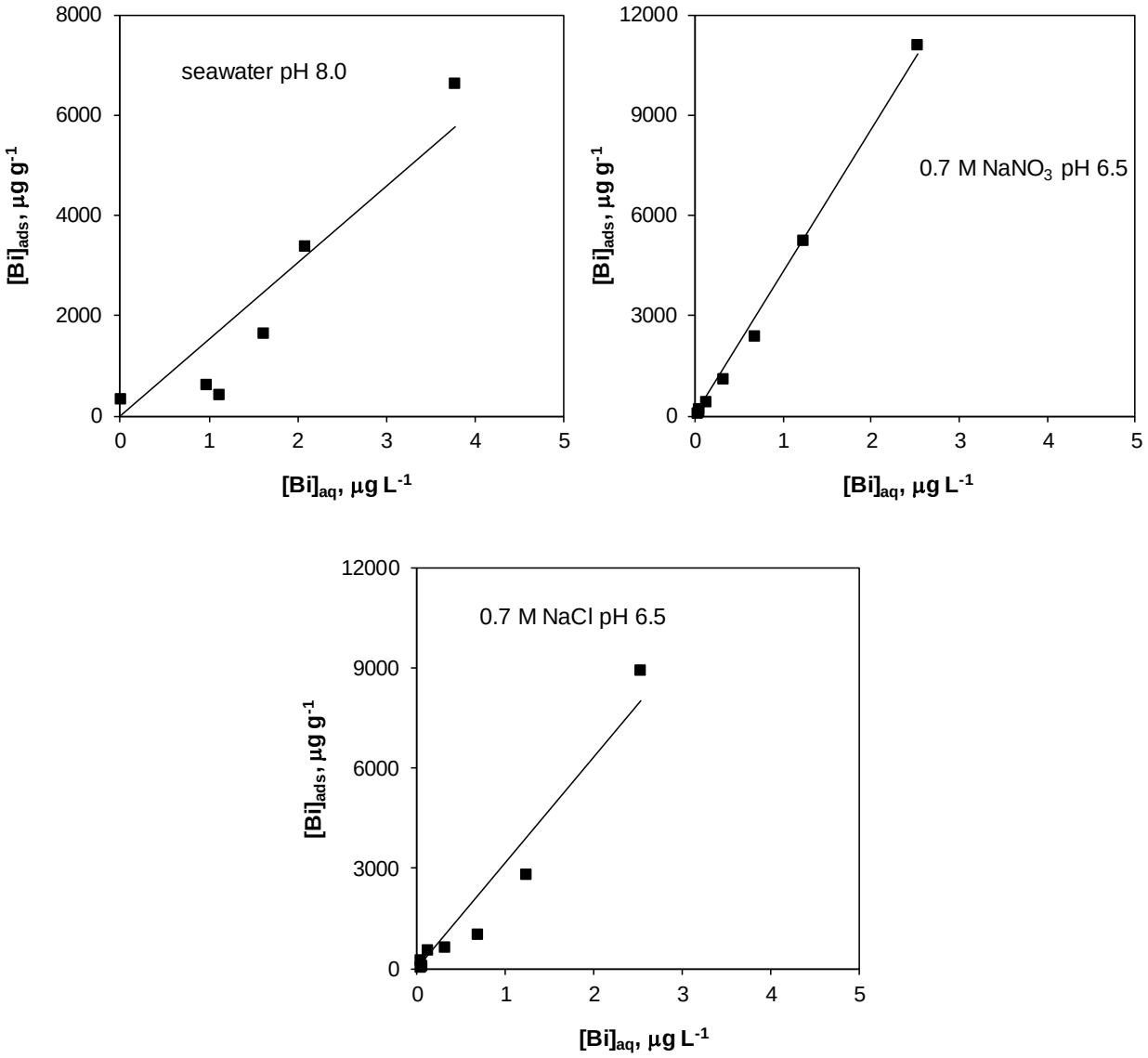

Figure 3: Logged sediment-water distribution coefficients for Bi (added at a concentration of 1000 μg L^{-1}) on mixing river water (pH 6.3) and seawater (pH 8.0) and shown as a function of salinity. The solid line denotes the best fit through the data with the equation, goodness of fit and significance annotated.

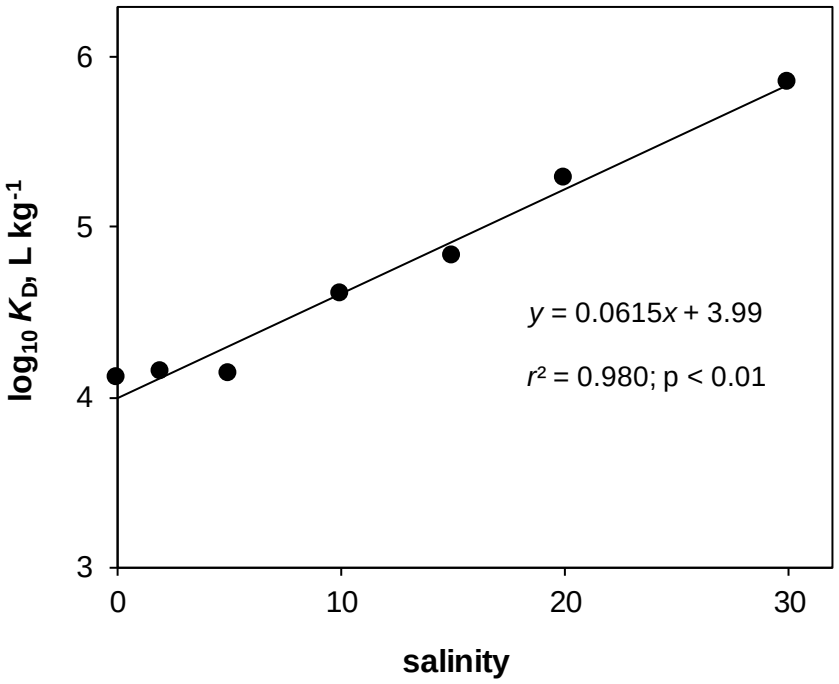

Figure 4: The percentage of Bi (added at a concentration of 1000 μg L^{-1}) retained on filters on mixing river water (pH 6.3) and seawater (pH 8.0) in the absence of estuarine sediment and shown as a function of salinity.

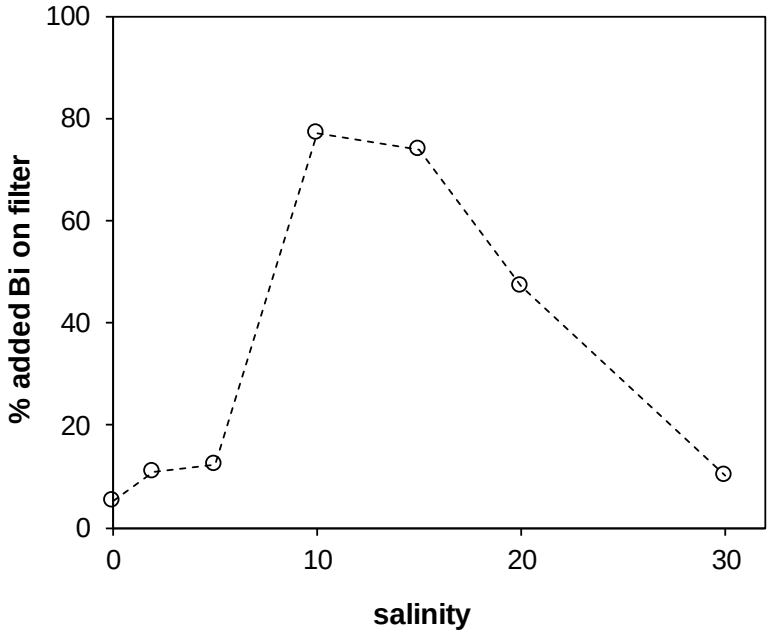

Figure 5: Logged sediment-water distribution coefficients shown in ascending order for different metals studied as tracers in (a) the River Plym (pH 6 to 7) or River Erme (Bi only) and (b) English Channel seawater (pH ~8). Data are taken from Table 2 and Turner (2007) and references therein.